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Coupled Hartree–Fock Calculations of Nuclear Magnetic Resonance Carbon–Carbon Coupling Constants in Substituted Benzenes

Paolo Lazzeretti,* Ferdinando Taddei, and Riccardo Zanasi

Contribution from Istituto di Chimica Organica, Università, 41100 Modena, Italy.

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Abstract: The coupled Hartree–Fock perturbation theory is applied, within the limits of INDO approximation, to compute direct and long-range coupling constants between ^{13}C nuclei in substituted benzenes. Contact, orbital, and dipolar terms are used throughout the calculations, showing that the Fermi contact is often insufficient to account for the observed couplings. Agreement with experimental data is quite satisfactory and much better than with other calculations. A preliminary determination of the parameters necessary in the semiempirical calculation afforded the values $s_C^2(0)s_C^2(0) = 13.5150$ au, $\langle r^{-3}\rangle_C\langle r^{-3}\rangle_C = 7.9832$ au.

The theory of nuclear spin–spin coupling has its roots in the pioneering work of Ramsey,[1,2] who showed that three distinct mechanisms concur in determining this interaction, namely the Fermi contact term, nucleus–nucleus dipolar interaction, and nuclear spin–electron orbit coupling. Ramsey tackled the problem of computing coupling constants measured in NMR spectroscopy by means of the conventional perturbation theory. Because of difficulties encountered in handling the second-order perturbation formula, McConnell introduced the closure approximation,[3] using an average excitation energy in his MOLCAO approach. Some authors, however, suggested that the use of mean energy approximation is far from valid, the convergence of the perturbation expansion needing to be carefully checked.[4,5] A refined MOLCAO procedure was introduced by Pople and Santry[6] which, by overcoming the average excitation energy approximation, provides improved results.

A more promising method was recently proposed by Pople et al.;[7] they put forward a "finite perturbation theory" (FPT) using a variational wave function which contained the perturbation explicitly. Nevertheless, the Hartree–Fock perturbation theory seems to provide more flexible and powerful methods of computing nuclear spin coupling constants: the coupled Hartree-Fock perturbation theory (CHFPT)[8] has been used to calculate the contact interaction by Power and Pitzer;[9] Blizzard and Santry[10] have evaluated the contributions of all three mechanisms studied by Ramsey allowing for the INDO approximation.[11] Ab initio calculations by Ditchfield and Snyder[12] are also available. These authors[10] show that dipolar and orbital terms are far from negligible in C–C, C–F, and F–F couplings.

In the present paper, CHFPT is applied to compute carbon–carbon coupling constants in substituted benzenes. Fermi contact, orbital, and dipolar terms are taken into account within the framework of INDO approximation. Some preliminary work is devoted to evaluating an empirical set of parameters to be used in the actual calculations: the necessary quantities are the electron density at carbon nucleus, $s_C^2(0)$, and the mean value $\langle r^{-3}\rangle_C$.

Outline of Calculation

The computational scheme employed is essentially the same as that used to evaluate electric polarizabilities and magnetic susceptibilities,[13] hence only master equations are referred to here, a more detailed treatment being available elsewhere.[8,13a] NMR reduced coupling constants between atoms A and B are defined as[6,14]

$$K_{\mathrm{AB}} = (2\pi/\hbar\gamma_{\mathrm{A}}\gamma_{\mathrm{B}})J_{\mathrm{AB}} \tag{1}$$

and can be given the general form

$$K_{\mathrm{AB}} = -2tr\mathbf{H}^{(1)}\mathbf{P}^{(1)} \tag{2}$$

where $\mathbf{H}^{(1)}$ is the matrix representative of a perturbing Hamiltonian and $\mathbf{P}^{(1)}$ is the Fock-Dirac density matrix at first-order in the perturbation.[8] Introducing a suitable set of projection operators,[8] $\mathbf{P}^{(1)}$ is resolved as

$$\mathbf{P}^{(1)} = \mathbf{X} + \mathbf{X}^{+} \tag{3}$$

with

$$\mathbf{X} = \sum_{i=1}^{n} \mathbf{c}_i^{(0)}\mathbf{c}_i^{(1)+} \tag{4}$$

expressed in terms of zero-order eigenvectors $\mathbf{c}_i^{(0)}$ and their first-order corrections

$$\mathbf{c}_i^{(1)} = \sum_{k=n+1}^{m} \frac{\mathbf{c}_k^{(0)+}\mathbf{F}^{(1)}\mathbf{c}_i^{(0)}}{\epsilon_i^{(0)} - \epsilon_k^{(0)}}\mathbf{c}_k^{(0)} \tag{5}$$

where $\mathbf{F}^{(1)}$ is the Hartree-Fock Hamiltonian at first order in the perturbation:

$$\mathbf{F}^{(1)} = \mathbf{H}^{(1)} + \mathbf{G}^{(1)} \tag{6}$$

Following Ramsey[1,2] the hyperfine Hamiltonian operator is

$$\mathcal{H}_{\mathrm{HFS}} = \sum_{N} \{\mathcal{H}_{\mathrm{F}}(N) + \mathcal{H}_{\mathrm{SO}}(N) + \mathcal{H}_{\mathrm{D}}(N)\} \tag{7}$$

where

$$\mathcal{H}_{\mathrm{F}}(N) = (16/3)\pi\beta \sum_{k} \delta(\mathbf{r}_{kN})\mathbf{S}_k \cdot \boldsymbol{\mu}_N \tag{8}$$

$$\mathcal{H}_{\mathrm{SO}}(N) = 2(\beta/\hbar) \sum_{k} r_{kN}^{-3}\boldsymbol{\mu}_N \cdot \boldsymbol{\mathcal{L}}_{kN} \tag{9}$$

$$\mathcal{H}_{\mathrm{D}}(N) = 2\beta \sum_{k} \{3r_{kN}^{-5}(\mathbf{S}_k \cdot \mathbf{r}_{kN})(\boldsymbol{\mu}_N \cdot \mathbf{r}_{kN}) - r_{kN}^{-3}(\mathbf{S}_k \cdot \boldsymbol{\mu}_N)\} \tag{10}$$

$$\boldsymbol{\mu}_N = \gamma_N\hbar\mathbf{I}_N;\ \mathbf{r}_{kN} = \mathbf{r}_k - \mathbf{r}_N;\ \boldsymbol{\mathcal{L}}_{kN} = \mathbf{r}_{kN} \times \mathbf{p}_k \tag{11}$$

Hamiltonian (eq 8) arises from the Fermi contact field around nucleus N, $\mathcal{H}_{\mathrm{SO}}$ accounts for nuclear spin-electron orbit interaction and $\mathcal{H}_{\mathrm{D}}$ is the Hamiltonian for dipolar interaction between nuclear magnetic moment $\boldsymbol{\mu}_N$ and the magnetic dipole of the kth electron, $\boldsymbol{\mu}_k = -2\beta\mathbf{S}_k$. Since the coupling tensor is defined[15] as the derivative of total molecular energy with respect to $\boldsymbol{\mu}_N$

$$W_{\sigma\tau} = \lim_{\mu \to 0} \left[-\frac{\partial^2 W}{\partial\mu_\sigma\partial\mu_\tau}\right] \tag{12}$$

$$W = W_0 - \mu_\sigma W_\sigma - (1/2!)\,\mu_\sigma\mu_\tau W_{\sigma\tau}^{(2)} + \ldots \tag{13}$$

adopting the summation convention,[15] one gets rid of μ, assumed to point in the z direction, by means of the Hellmann-Feynman theorem, defining the model Hamiltonian

$$H_{\mathrm{HFS}} = \partial\mathcal{H}_{\mathrm{HFS}}/\partial\mu \tag{14}$$

which contains pure electronic operators. Since $\boldsymbol{\mu}_N$ is a nuclear operator, total energy (eq 13) becomes an operator in nuclear space, and this procedure can be referred to as a reduction to μ subspace. Now the reduced hyperfine Hamiltonian (eq 14) can be dealt with as a perturbation to Hartree-Fock Hamiltonian in order to apply the CHFPT scheme. Since the first-order repulsion $\mathbf{G}^{(1)}$ in eq 6 is a function of $\mathbf{P}^{(1)}$, eq 2-6 must be solved iteratively starting with $\mathbf{G}^{(1)} = \mathbf{0}$ in eq 6. In the calculations reported in this paper, the INDO approximation is retained at zero and first order. Since Hamiltonian (eq 8) induces spin polarization, the Pople-Nesbet unrestricted HF scheme[16] is employed to evaluate the isotropic Fermi contact contributions, and the following formulas are obtained for α electrons:[10]

$$\mathrm{H}^{(\alpha)} = \mathbf{0},\ \text{except } \mathrm{H}_{s_{\mathrm{A}}s_{\mathrm{A}}}{}^{(\alpha)} = (8/3)\pi\beta s_{\mathrm{A}}{}^2(0);\ \text{scaled to 1 in actual calculations} \tag{15}$$

$$G_{\sigma\sigma}{}^{(\alpha)} = -\sum_{\lambda} P_{\lambda\lambda}{}^{(\alpha)}[\sigma\lambda|\sigma\lambda];\quad \sigma \text{ and } \lambda \text{ both on the same atom} \tag{16}$$

$$G_{\sigma\nu}{}^{(\alpha)} = -P_{\sigma\nu}{}^{(\alpha)}\{[\sigma\nu|\sigma\nu] + [\sigma\sigma|\nu\nu]\};\quad \sigma \neq \nu \text{ both on the same atom} \tag{17}$$

$$G_{\sigma\nu}{}^{(\alpha)} = -P_{\sigma\nu}{}^{(\alpha)}[\sigma\sigma|\nu\nu];\ \sigma \neq \nu \text{ on different atoms} \tag{18}$$

$$-\mathbf{P}^{(\beta)} = \mathbf{P}^{(\alpha)} = \mathbf{X}^{(\alpha)} + \mathbf{X}^{(\alpha)+};\ \mathbf{J}^{(\alpha)} = -\mathbf{J}^{(\beta)} \tag{19}$$

$$K_{\mathrm{AB}} = 2P_{s_{\mathrm{B}}s_{\mathrm{B}}}{}^{(\alpha)}(8\pi\beta/3)^2 s_{\mathrm{A}}{}^2(0)s_{\mathrm{B}}{}^2(0) \tag{20}$$

where eq 19 shows that it is necessary to solve the CHFPT problem only for the α perturbation.

For the spin-orbit interactions, similar equations are found to hold;[10] assuming μ_N in the z direction, ($\mathbf{C}^{(1)}$, $\mathbf{P}^{(1)}$, $\mathbf{F}^{(1)}$ pure imaginary), $\mathbf{J}^{(1)} \approx \mathbf{0}$

$$\mathbf{H}^{(1)} = \mathbf{0},\ \text{except } H_{x_{\mathrm{B}}y_{\mathrm{B}}}{}^{(1)} = H_{y_{\mathrm{B}}x_{\mathrm{B}}}{}^{(1)} = -i(2\beta)\ \langle r^{-3}\rangle_{\mathrm{B}};\ \text{scaled to 1 in actual calculations} \tag{21}$$

$$G_{\sigma\sigma}{}^{(1)} = 0 \tag{22}$$

$$G_{\sigma\nu}{}^{(1)} = -(1/2)P_{\sigma\nu}{}^{(1)}\{[\sigma\sigma|\nu\nu] - [\sigma\nu|\sigma\nu]\};\quad \nu \neq \sigma \text{ both on the same atom} \tag{23}$$

$$G_{\sigma\nu}{}^{(1)} = -(1/2)P_{\sigma\nu}{}^{(1)}[\sigma\sigma|\nu\nu];\ \nu \neq \sigma \text{ on different atoms} \tag{24}$$

$$\mathbf{P}^{(1)} = \mathbf{P}^{(1)+} \tag{25}$$

$$K_{\mathrm{AB}} = 2P_{x_{\mathrm{B}}y_{\mathrm{B}}}{}^{(1)}(2\beta)^2\langle r^{-3}\rangle_{\mathrm{A}}\langle r^{-3}\rangle_{\mathrm{B}} \tag{26}$$

The dipolar term is somewhat more complicated to handle, since it induces the mixing of α and β characters in a perturbed molecular orbital. Thus, the unrestricted HF scheme is redeveloped according to Blizzard and Santry[10] in terms of linear combinations of atomic spin orbitals (LCASO), and the fundamental quantities appearing in the HF theory must explicitly contain α and β cross terms, e.g., every matrix is partitioned into four submatrices.

$$\mathbf{M} = \begin{bmatrix} \mathbf{M}^{(\alpha\alpha)} & \mathbf{M}^{(\alpha\beta)} \\ \mathbf{M}^{(\beta\alpha)} & \mathbf{M}^{(\beta\beta)} \end{bmatrix} \tag{27}$$

The first-order density submatrices satisfy the following equations:

$$\mathbf{P}^{(\alpha\alpha)} = -\mathbf{P}^{(\beta\beta)};\quad \mathbf{P}^{(\alpha\beta)} = \mathbf{P}^{(\beta\alpha)+} \tag{28}$$

and for the Coulomb repulsion we have

$$\mathbf{J}^{(\alpha\alpha)} = -\mathbf{J}^{(\beta\beta)};\quad \mathbf{J}^{(\alpha\beta)} = \mathbf{J}^{(\beta\alpha)} = \mathbf{0} \tag{29}$$

so that the first-order HF Hamiltonian can be partitioned as

$$\mathbf{F}^{(\mu\nu)} = \mathbf{H}^{(\mu\nu)} - \mathbf{K}^{(\mu\nu)};\quad \mu,\nu = \alpha,\beta \tag{30}$$

where $\mathbf{H}^{(\mu\nu)}$ is the matrix representation of the spin-dipolar Hamiltonian in the LCASO basis and the first-order exchange interactions are

$$K_{\sigma\tau}{}^{(\mu\nu)} = \sum_{\theta\lambda} P_{\lambda\theta}{}^{(\mu\nu)}[\sigma\lambda|\theta\tau] \tag{31}$$

For the $(\alpha\alpha)$ and $(\beta\beta)$ contributions

$$\mathbf{H}^{(\alpha\alpha)} = \mathbf{0}, \text{ except } H_{z_A z_A}{}^{(\alpha\alpha)} = (4/5)\beta\langle r^{-3}\rangle_A;$$

$$H_{x_A x_A}{}^{(\alpha\alpha)} = H_{y_A y_A}{}^{(\alpha\alpha)} = -(2/5)\beta\langle r^{-3}\rangle_A$$

$$\text{scaled by the factor } \beta\langle r^{-3}\rangle_A \text{ in the calculations} \quad (32)$$

The matrices $\mathbf{G}^{(\alpha\alpha)}$ and $\mathbf{P}^{(\alpha\alpha)}$ are exactly the same as given in eq 16–18 for the contact field and

$$K_{AB} = (4/5)\beta^2(2P_{z_B z_B}{}^{(\alpha\alpha)} - P_{x_B x_B}{}^{(\alpha\alpha)} - P_{y_B y_B}{}^{(\alpha\alpha)})\langle r^{-3}\rangle_A\langle r^{-3}\rangle_B \quad (33)$$

For the $(\alpha\beta)$, $(\beta\alpha)$ real contributions

$$\mathbf{H}^{(\beta\alpha)} = \mathbf{0}, \text{ except } H_{x_A z_A}{}^{(\beta\alpha)} = H_{z_A x_A}{}^{(\beta\alpha)} = (3/5)\beta\langle r^{-3}\rangle_A; \text{ scaled to } 3/5 \quad (34)$$

$$K_{AB} = (12/5)\beta^2 P_{x_B z_B}{}^{(\alpha\beta)}\langle r^{-3}\rangle_A\langle r^{-3}\rangle_B \quad (35)$$

The matrix $\mathbf{G}^{(\alpha\beta)}$ is given by eq 16–18 and the real density matrix satisfies eq 28.

For the pure imaginary $(\alpha\beta)$, $(\beta\alpha)$ contributions

$$\mathbf{H}^{(\beta\alpha)} = \mathbf{0}, \text{ except } H_{y_A z_A}{}^{(\beta\alpha)} = H_{z_A y_A}{}^{(\beta\alpha)} = i(3/5)\beta\langle r^{-3}\rangle_A; \text{ scaled to } 3/5 \quad (36)$$

$$K_{AB} = -(12/5)\beta^2 P_{y_B z_B}{}^{(\alpha\beta)}\langle r^{-3}\rangle_A\langle r^{-3}\rangle_B \quad (37)$$

The matrix $\mathbf{G}^{(\beta\alpha)}$ is still evaluated via eq 16–18 and the pure imaginary density matrix $\mathbf{P}^{(\alpha\beta)}$ satisfies eq 28, so that, as with the real part, we need to solve only the problem for $(\beta\alpha)$ submatrices.[17]

To sum up, the CHFPT eq 3–6 are solved once for the isotropic Fermi interaction, three times (for nuclear spin in x, y, and z direction) to obtain the average orbital term, three times for the $(\alpha\alpha)$ submatrices (still assuming the perturbing spin in the x, y, and z directions), and three times for the $(\alpha\beta)$ real and imaginary perturbations. In fact, the equations for $(\alpha\beta)$ imaginary contributions need to be solved if one is interested in average coupling, for, allowing for the scaling procedure, the average $(\alpha\beta)$ component of dipolar coupling given by the imaginary part is equal to the average real $(\alpha\beta)$ contributions, as can be seen by inspection of eq 34 and 36. These partial contributions are sufficient to characterize the second-rank coupling tensor which describes anisotropic orbital and dipolar interactions. One accounts for rotational averaging by taking one-third of the trace of these tensors.

A computer program capable of performing the CHFPT computations was written for a CDC-CYBER 76 computer. Since the calculation procedure is particularly lengthy and time consuming, a careful optimization of the program, as well as numerical implementation of eq 3–6, was necessary in order to save computer time. Moreover, the number of iterations necessary to achieve convergence is dramatically high, so that suitable extrapolation and damping procedures were applied. The integrals $s_N{}^2(0)$, $\langle r^{-3}\rangle_N$ appearing in eq 15 and 21 are treated as adjustable parameters and estimated empirically, the best agreement, in the least-squares sense, being sought between a set of computed and experimental coupling constants.

Since the calculations of ref 10 are affected by a minor systematic error, we attempted to refit the experimental data for C–C, C–F, and F–F in our least-squares analysis. The parameters for carbon–carbon coupling and related coupling constants are reported in Table I.

The reviewed parameters are somewhat different from those given in ref 10 and the agreement between experimental and computed values is generally better. As expected, the main feature of these calculations is that the dipolar term is roughly twice that computed by Blizzard and Santry[10] (their results ought to be multiplied by a factor of 2 owing to a programming error). As a result, both the orbital contributions, which are mainly of negative sign, and the contact are also changed. Anyway, the overall trend obtained in ref 10 is confirmed and the conclusions contained therein are generally restated; e.g., as a rule, the inclusion of orbital and dipolar terms improves computed values, particularly for couplings involving double and triple carbon–carbon bonds, whereas, for saturated molecules, the contact term alone is often sufficient to explain experimental data and the minor orbital and dipolar contributions can be reasonably neglected. Our parameters also differ from those quoted in an earlier paper by Pople and Santry[6] and are somewhat larger than the atomic values.[20] On the other hand, the parameters employed in the present paper are expected to afford a more reliable description of the coupling in a molecular environment.

Table I. Calculated and Experimental Carbon-Carbon Coupling Constants in Structurally Different Organic Molecules ($s_C{}^2(0)s_C{}^2(0) = 13.5150$ au; $\langle r^{-3}\rangle_C\langle r^{-3}\rangle_C = 7.9832$ au)

Molecule	Contact	Orbital	Dipolar	Total	Exptl[a]
$C_6H_5C^*C^*H$	129.96	21.19	15.48	166.63	175.9
C_2H_2	136.14	22.72	16.00	174.86	171.5
$C_6{}^*H_5C^*N$	73.83	−2.25	1.49	73.07	80.40
$C^*H_2C^*HCN$	67.35	−17.71	7.53	57.17	70.6
C_2H_4	68.27	−17.89	7.55	57.93	67.6
$C^*H_3C^*CH$	64.33	−2.55	1.02	62.80	67.4
C_6H_6	63.13	−12.28	3.00	53.85	57.0
CH_3COOH	71.55	−2.69	1.14	70.00	56.7
CH_3CN	63.77	−2.46	1.10	62.41	56.5
$CH_3C^*H_2C^*N$	63.37	−2.66	0.89	61.60	55.2
CH_3CO^+	52.43	−6.40	−0.19	45.84	46.5
$C^*H_3C^*OCH_3$	54.29	−2.81	1.41	52.88	40.1
CH_3CHO	58.29	−3.07	1.37	56.59	39.4
C_2H_6	34.45	−2.80	1.41	33.05	34.6
$C^*H_3C^*H_2CN$	33.81	−2.39	1.52	32.94	33.0
CH_3CH_2OH	38.66	−2.75	1.58	37.49	37.7[b]

[a] Experimental values quoted in ref 10. [b] Reference 27.

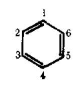
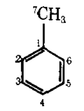
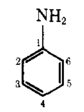
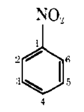
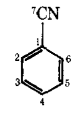
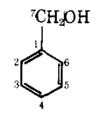
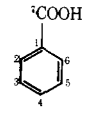
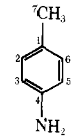
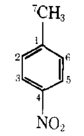
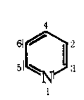
Results and Discussion

The new parameters are used to evaluate the C–C coupling for a series of substituted benzenes and related molecules. The main concern here is the calculation of directly bonded C–C coupling constants, for which fuller experimental information is available.[21,7c] Some attempts are also made to test the reliability of the INDO–CHFPT approach to long-range couplings, including those between a substituent and a ring carbon. Molecular geometries used in the calculation are mainly taken from Sutton's tables,[22] with a few exceptions, e.g., idealized bond lengths and angles are assumed for benzoic acid and benzylic alcohol. Moreover, such calculations are carried out on what is considered to be the preferred conformation of substituents in the ring. In our experience, slightly different results can be obtained if these conformations are varied, but computed results do not appear to be critically dependent on the geometrical arrangement assumed for the molecule. As regards directly bonded carbon atoms, the calculated values are positive, in agreement with Grant's determination[23] of J_{CH} and J_{CC} relative signs in acetic acid, as well as other calculations.[7c,24,25]

Total computed values are in good agreement with experimental data and seem to rationalize measured data more accurately than other calculations by Pople and co-workers,[7c] who largely overestimate the coupling (roughly by an amount of 20 Hz), taking into account the Fermi contact alone.

Since the theoretical approach furnished by FPT[7] is equivalent to CHFPT, these results show that, besides the discrepancies in the parameter set, the inclusion of the orbital and dipolar term is of critical importance if the coupling mechanism in substituted benzenes is to be understood. According to our calculations, the orbital contributions are neg-

Table II. Calculated and Experimental Carbon–Carbon Coupling Constants in Substituted Benzenes[e]

Molecule									
	J_{1-2}	J_{1-3}	J_{1-4}						
	63.13	−9.03	9.58						
	−12.28	0.87	0.96						
	3.00	−2.46	3.78						
	53.85	−10.62	14.32						
	(57.0)[a]								
	J_{1-2}	J_{1-3}	J_{1-4}	J_{1-7}	J_{2-7}	J_{3-7}	J_{4-7}		
	60.91	−8.15	9.37	40.30	−4.70	4.20	−1.80		
	−12.43	0.81	0.96	−2.80	0.21	0.06	−0.05		
	2.93	−2.40	3.78	1.37	−0.08	0.12	−0.12		
	51.41	−9.74	14.11	38.87	−4.57	4.38	−1.97		
	(57.3)[b]	(0.8)[b]	(9.4)[b]	(44.19)[b]	(3.10)[c]	(3.84)[c]	(0.86)[c]		
	J_{1-2}	J_{1-3}	J_{1-4}	J_{2-3}	J_{2-4}	J_{2-5}	J_{2-6}	J_{3-4}	J_{3-5}
	66.48	−7.21	9.04	63.01	−9.23	8.95	−7.20	63.62	−8.91
	−11.13	0.76	0.84	−12.55	0.74	0.84	0.86	−12.07	0.92
	2.75	−2.17	3.45	3.13	−2.65	3.79	−2.45	3.11	−2.47
	58.10	−8.62	13.33	53.59	−11.14	13.58	−8.79	54.66	−10.46
	(61.3)[a]			(58.1)[a]				(56.2)[a]	
	J_{1-2}	J_{1-3}	J_{1-4}	J_{2-3}	J_{2-4}	J_{2-5}	J_{2-6}	J_{3-4}	J_{3-5}
	65.53	−9.08	8.88	61.77	−8.96	9.32	−7.65	63.39	−9.84
	−11.39	0.82	0.83	−12.95	0.97	0.90	0.49	−11.89	1.07
	2.64	−2.16	2.84	3.21	−2.26	4.09	−2.67	2.82	−2.68
	56.78	−10.42	12.55	52.03	−10.25	14.31	−9.83	54.32	−11.45
	(55.4)[a]			(56.3)[a]				(55.8)[a]	
	J_{1-2}	J_{1-3}	J_{1-4}	J_{1-7}	J_{2-7}	J_{3-7}	J_{4-7}		
	59.99	−7.66	9.37	73.83	−7.48	6.27	−2.75		
	−12.20	0.74	1.00	−2.25	1.41	−0.01	−0.16		
	2.82	−2.32	3.72	1.49	−0.68	0.59	−0.86		
	50.61	−9.24	14.09	73.07	−6.75	6.85	−3.77		
				(80.40)[c]	(2.61)[c]	(5.75)[c]	(1.59)[c]		
	J_{1-2}	J_{1-3}	J_{1-4}	J_{1-7}	J_{2-7}	J_{3-7}	J_{4-7}		
	61.05	−8.25	9.52	55.27	−6.51	6.06	−3.09		
	−12.38	0.78	0.99	−2.95	0.43	0.06	−0.04		
	2.82	−2.34	3.71	1.30	−0.30	0.29	−0.36		
	51.49	−9.81	14.22	53.62	−6.38	6.41	−3.49		
				(47.72)[c]	(3.45)[c]	(3.95)[c]	(0.73)[c]		
	J_{1-2}	J_{1-3}	J_{1-4}	J_{1-7}	J_{2-7}	J_{3-7}	J_{4-7}		
	58.02	−8.43	9.37	78.85	−6.61	5.40	−1.82		
	−12.47	0.82	0.98	−2.68	0.36	0.00	0.05		
	2.85	−2.36	3.73	0.73	0.04	0.04	−0.03		
	48.40	−9.97	14.08	76.90	−6.21	5.44	−1.80		
				(71.87)[c]	(2.54)[c]	(4.53)[c]	(0.90)[c]		
	J_{1-2}	J_{1-3}	J_{1-4}	J_{1-7}	J_{2-7}	J_{3-7}	J_{4-7}		
	61.49	−8.42	9.00	40.93	−4.75	4.36	−1.60		
	−12.28	0.59	0.84	−2.82	0.23	0.07	−0.04		
	3.10	−2.68	3.52	1.36	−0.09	0.13	−0.11		
	52.31	−10.51	13.36	39.47	−4.61	4.56	−1.75		
				(45.91)[d]	(3.17)[d]	(4.19)[d]	(0.56)[d]		
	J_{1-2}	J_{1-3}	J_{1-4}	J_{1-7}	J_{2-7}	J_{3-7}	J_{4-7}		
	59.96	−8.28	9.66	40.01	−4.46	4.22	−1.90		
	−12.37	1.11	0.97	−2.90	0.19	0.07	−0.05		
	2.82	−2.30	3.58	1.36	−0.08	0.12	−0.11		
	50.41	−9.47	14.22	38.47	−4.35	4.41	−2.06		
				(43.45)[d]	(3.46)[d]	(3.87)[d]			
	J_{2-3}	J_{2-4}	J_{2-5}	J_{2-6}	J_{3-4}	J_{3-5}			
	69.00	−10.59	11.61	−18.90	61.06	−9.32			
	−11.99	1.15	1.30	1.03	−12.23	1.03			
	3.57	−3.11	4.28	−3.29	3.27	−2.65			
	60.58	−12.55	17.19	−21.16	52.10	−10.94			
	(53.8)[a]				(53.8)[a]				

[a] Reference 7c. [b] Reference 21b. [c] Reference 21c. [d] Reference 21a. [e] For each molecule rows refer, in order, to contact, orbital, dipolar terms, and total calculated coupling constants; experimental values are reported in parentheses.

ative and counterbalance the positive Fermi contact. It can be calculated that these contributions affect total computed values by up to 20%. On the other hand, the dipolar term is found to be rather small, its contribution to the total computed value being roughly 5%. They would therefore appear to be negligible, and, in view of their troublesome calculation, it seems reasonable to ignore them.

Another interesting pattern obtained from inspection of the tables is that, irrespective of the substituent type and its location relative to coupling carbons, the calculated contributions cover a narrow range of values, which seems to indicate that coupling between benzenic directly-bonded carbon nuclei is mainly determined by the geometric structure of the ring and its general chemical characteristics. In fact, these results seem insensitive to a peculiar chemical environment or substituent; the Fermi contact ranges from about 60 to 70 Hz, the orbital term is almost a constant value of 12 Hz, while the dipolar contributions range between 1.5 and 3 Hz for all the aromatic couplings studied. This is in contrast with the larger range of values, also satisfactorily reproduced in these calculations, from ethane to acetylene.

As regards direct coupling between an aromatic carbon and a substituent carbon, e.g., toluene, only a few experimental data are available,[21] but here again the agreement with computed values is fairly good. In this case the coupling is more closely dependent on the nature of the substituent and the overall behavior is well interpreted in terms of the electronic characteristics of the substituent itself: computed constants increase as the electronegativity of the carbon atom in the substituent increases, and this effect is several times larger for the carbonyl group, which is likely to be due to its polarizability.[21a] Moreover, these couplings are evidently influenced by the resonance effects of the various substituents, which is correctly predicted by the calculations. The observed trend is also consistent with earlier empirical correlations in terms of orbital hybridization.[21a] In these couplings the Fermi contact alone is sufficient to rationalize the experimental data, since the small negative orbital and positive dipolar terms almost compensate each other; thus, in future calculations, only the contact field can be reasonably retained.

Experimental long-range couplings between ring carbons are lacking and it is difficult to assess the reliability of computed values. In toluene, the computed and measured J_{1-4} compare quite well (14.11 against 9.4 Hz, Table II), but the prediction for J_{1-3} seems very far from accurate ($\sim$10 against $\sim$1 Hz). In this case, too, CHFPT yields results which are almost constant in the series studied here, e.g., about 10 Hz for meta couplings and about 14 Hz for para couplings, thus showing a marked dependence on the coupling pathway. The negligible size of the orbital and dipolar contributions suggests that the contact term alone probably accounts for the total contribution observed. A knowledge of these couplings would enable one to understand not only how spin information is transmitted in the ring, but also the role played by σ and π electrons; unfortunately, the paucity of experimental data precludes any such possibility. On the other hand, experimental data are availble for long-range couplings between the substituent and ring carbons[21] and are in good agreement with the values provided by INDO-CHFPT. The calculations give a negative sign for 2–7 and 4–7 interactions, but 3–7 interactions are positive for all the molecules studied. It is hoped that these notes might be useful for other purposes, since direct experimental determination of sign is difficult.

The magnitude of J's measured decreases rapidly passing from 1-7 to 4-7 interactions, as do computed couplings, thus giving a further proof of the reliability of the computational method. Only the remote 4-7 couplings are systematically overestimated.

An interesting feature of measured aromatic long-range couplings is that the three-bond J_{3-7} is larger than the two-bond J_{2-7}, even if they are close together. As a rule, with the exception of -CN and -CH_2OH substituents, the INDO-CHFPT fails to predict this remarkable fact.

Summary and Conclusions

The calculations reported here show that CHFPT, within the framework of INDO approximation, successfully accounts for the experimental coupling constants of substituted benzenes. The least-squares optimized parameters adopted here can be used to predict a wide range of data (about 150 Hz from ethane to acetylene). The method would appear to be of considerable assistance in predicting the absolute value and sign of the coupling of aromatic molecules and in assessing the importance of usually neglected orbital and dipolar contributions, particularly in the case of directly bonded carbon atoms. The calculations indicate, however, that the Fermi contact alone can be reasonably successful in predicting long-range couplings, and this must be borne in mind in order to save computer time and to avoid unnecessary calculations. On the other hand, the limitations of this method are quite evident: within the framework of the semiempirical INDO approximation, the representation of the hyperfine Hamiltonian is extremely poor, see eq 15, 21, 32, 34, which is also revealed by the high number of iterations necessary to get convergence. This fact suggests that the method could be significantly improved assuming more reliable representations of first-order $\mathbf{H}^{(1)}$ matrix,[26] possibly beyond the INDO approximation for integrals. A considerable simplification of the computation procedure could be obtained by uncoupling the perturbation equations,[13a] which would allow a substantial saving of computer time.

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